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EVALUATION OF REGENERATIVE FUEL CELL

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Prepared by
Harvey A. Frank
Harvey A. Frank
Project Supervisor

Approved by
CW Stephens
C.W. Stephens
Acting Manager
Chemical Systems Department

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Approved by

CW Stephens

for J. Neustein, Manager
ADVANCED POWER SYSTEMS DIVISION

CONTENTS

	<u>Page</u>
1. SUMMARY	1
2. REVIEW OF OBJECTIVES	5
3. SUMMARY OF EXPERIMENTAL PROGRAM	7
4. EXPERIMENTAL TECHNIQUES	9
4.1 Electrode Preparations	9
4.1.1 Preparation of Platinized Nickel Electrodes	9
4.1.2 Radioactive Electrodes	9
4.1.3 Preparation of Carbon Electrodes	9
4.1.4 Preparation of Lithiated Nickel Oxide Electrodes	11
4.2 Electrolyte Preparation	11
4.3 Spacers for Multicell	13
4.4 Assembly of Multicell	13
4.5 Temperature, Pressure, and Voltage Measurements	13
4.6 Polarization Tests	13
4.7 Conduct of Charge Retention Tests	14
4.8 Conduct of Cycle Tests	14
5. DESCRIPTION OF EXPERIMENTAL CELLS	15
5.1 Description of Cell A	15
5.2 Description of Cell B	17
5.3 Description of Multicell	19
5.4 Description of Ag-H Cell	23
6. RESULTS AND DISCUSSION	25
6.1 Characteristics of Cell A	25
6.1.1 Polarization Characteristics	25
6.1.2 Cycle Life	25
6.1.3 Effect of Parameters on Cycling Performance	25

CONTENTS (cont)

	<u>Page</u>
6.2 Characteristics of Cell B	26
6.2.1 Charge Retention	26
6.2.2 Polarization Studies	29
6.2.3 Cycle Life Testing	33
6.2.4 Capacity	35
6.2.5 Environmental Testing	36
6.2.6 Effect of Overcharge	39
6.2.7 Effect of Sudden Pressure Release	40
6.2.8 Effect of Pressure Differential	41
6.2.9 Multicell	42
6.3 Characteristics of Cell C	45
7. CONCLUSIONS	47
REFERENCES	49

ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1	Controlled atmosphere furnace for electrode preparation	12
2	Components of cell A	16
3	Components of cell B	18
4	Six cell assemblies	18
5	Cell spacer	20
6	Multi-cell assembly	20
7	Nine element fuel cell	21
8	Schematic of silver hydrogen cell	22
9	Voltage-current curves of cell A	24
10	30 day charge retention test	27
11	Discharge characteristics after 30 day stand	27
12	Charge retention as a function of temperature at various pressures	28
13	Oxygen electrode evaluation	31
14	Effect of pressure on polarization	32
15	Effect of temperature on discharge polarization	32
16	Typical 65/35 cycle at 70°F	34
17	Typical 60/300 cycle	34
18	Typical 65/35 cycle at 200°F	34
19	Voltage vs time before and after environmental tests	37
20	Polarization before and after environmental tests	37
21	Discharge characteristics after overcharge	38
22	Voltage vs time as a function of temperature	43
23	Polarization of 9 cell unit	43

1. SUMMARY

The objective of this program has been to develop and evaluate the characteristics of a regenerative hydrogen-oxygen fuel cell.

The initial experimental program was concerned with the evaluation of the proposed cell. This cell was unique in the method of storing the gases; i.e. hydrogen was stored within a porous nickel electrode in the chemisorbed state and oxygen was stored as a compressed gas in the pores of its electrode as well as the pores of a partially saturated asbestos bed surrounding the two electrodes. The cell was also unique in that its operating temperature range was 200 to 300°F. The investigations consisted initially of evaluating the effects of the controllable parameters (temperature, electrolyte content, and electrode composition) on the voltage and current efficiencies for the 100 minute cycle (consisting of a 65 minute charge and a 35 minute discharge). Subsequent investigations consisted of the determination of the cell's voltage-current characteristics, capacity, and charge retention characteristics.

The latter investigations indicated that the proposed cell configuration was unsuitable as the results revealed that this cell lost nearly all of its charge in two hours. Analysis of the possible cause for the rapid self discharge indicated that the rate might be lessened by modifying the cell configuration and storing the gases in separate containers. Inspection of the fuel cell literature also indicated that operation at room temperature would be possible if the negative nickel electrode were to be activated with a coating of platinum black.

Fabrication and testing of a cell with the above modifications established that the self discharge rate was markedly reduced and that the cell could deliver reasonable currents at room temperature. The experimental effort for the balance of the program was devoted to the development and testing of this cell.

The self discharge rate was measured over a wide range of temperatures to 300°F and pressures to 500 psig. The rate was found to be a very strong function of temperature beyond 200°F and nearly independent of pressure to 500 psig. The rate was found to be essentially zero at all temperatures below 170°F.

The cell's voltage-current characteristics were determined as a function of over 30 different types of oxygen electrodes with a platinized nickel hydrogen electrode. One of these oxygen electrodes, a radioactive treated electrode from a battery supplier, was found to exhibit significantly less polarization than all of the others. The polarization with a platinized nickel oxygen electrode was found to be somewhat greater than that with the radioactive electrode, but somewhat less than most of the others. With platinized nickel for both H₂ and O₂ the voltage-current characteristics were determined as a function of pressure and temperature.

Three cycle life tests were initiated and are in progress at the writing of this report. One cell has successfully completed over 1100 shallow cycles consisting of a 65 minute charge at 0.125 amp and a 35 minute discharge at 0.200 amp at room temperature. Another cell has successfully completed over 150 of the same cycles at 200°F. A third has successfully completed 70 deep cycles consisting of a 60 minute charge at 1.0 amp and a 300 minute discharge at 0.2 amp at room temperature.

Additional investigations on this cell include the effect of vibration, shock, and acceleration on performance. The safety hazards involved in excessive overcharging and the sudden release of pressure of one gas were also investigated. None of the above environmental tests were found to have any effect on performance and no apparent safety hazards are involved in the operation of the cell.

Development and testing of a 9 cell unit was successfully completed during the latter portion of the program. The cylindrical shaped unit, 6 inches by 8 inches long, has a total weight of 10.5 lbs. The fuel cell

portion of the unit contributes 2.0 lbs. and the balance is due to the gas cylinders, end plates, etc. The unit can deliver up to 25 watts.

Preliminary evaluation of a "silver-hydrogen" cell was also carried out during the latter portion of the program. Based on the first test results the system offers a potentially high power efficiency of over 90 percent.

Future work in this program should be devoted to the further development of the multicell. The unit should be redesigned so as to reduce overall weight, heat transfer studies should be carried out to determine the required insulation necessary for a given operating temperature. Additional units may then be designed for given applications, fabricated, and tested.

2. REVIEW OF OBJECTIVES

The overall objectives of this program have been to develop and then evaluate the characteristics of a regenerative hydrogen-oxygen fuel cell.

The specific objectives for each quarter have been as follows:

1st quarter

The objective was to design and fabricate a corrosion proof leak tight cell and assemble all measuring equipment.

2nd quarter

The objective was to investigate the effects of all the controllable parameters on the voltage and current efficiency of this cell for the 65/35 cycle.

3rd quarter

The objective was to complete the parametric study which had been initiated during the 2nd quarter. An additional objective was to measure the charge retention characteristics of this cell and examine the factors which affected this characteristic.

4th quarter

The charge retention studies in the 3rd quarter revealed that the charge retention of the cell was very low. The studies also revealed that if a certain modification were made in the cell configuration, then the charge retention was greatly increased. Another finding during this quarter was that the use of different types of electrodes permitted operation at lower temperatures. The objective during the 4th quarter then was to construct two additional cell models with the above modifications and measure the charge retention at various conditions of temperature and pressure. Another objective was to begin a search for improved oxygen electrodes which would lower the cell polarization at the lower temperatures.

5th quarter

The objective was to continue the evaluation of the modified cell. The evaluation of the effects of temperature and pressure on charge retention was to be continued. In addition the evaluation was to consist of a study of the effects of continued cycling on performance. The oxygen electrode evaluation was to be continued and the design of a multicell unit was to be initiated.

6th quarter

The objective was to continue the evaluation of the modified cell. Special emphasis was to be placed on the development of the multicell unit. The charge retention, cycle life, and polarization studies were to be continued.

3. SUMMARY OF EXPERIMENTAL PROGRAM

During the first six months of this program the experimental effort was concerned with the evaluation of the proposed cell configuration. The initial step consisted of developing a leak proof, corrosion resistant version of the proposed cell. Next the techniques were devised for preparing lithiated nickel oxide electrodes. Three constant current power supplies with automatic cycling were assembled and several exploratory runs were carried out. Three identical cells were machined and a variable study was initiated.

The next three months were devoted exclusively to this variable study in which the effects of temperature, electrolyte content, and electrode composition on the cell performance were evaluated.

Near the end of this study it was found that another cell characteristic, that of charge retention, was relatively low. Analysis of the cause for high self discharge indicated that improved charge retention characteristics should be brought about by modification of the existing cell configuration. Fabrication and testing of the modified cell confirmed that the high self discharge was markedly reduced. Additional findings at this time revealed that the operating range of the cell could be extended to lower temperatures, via the use of platinized nickel electrodes.

Two additional cells with the above modifications were fabricated and subjected to various tests. Additional data was obtained on charge retention, voltage-current relationship, capacity, and cycling characteristics.

During the last six months four additional models were fabricated and extensive testing was carried out. Over 50 charge retention tests were conducted at various conditions of temperature to 300°F and pressure to 500 psig. (In a number of the initial tests gas leaks developed in the tubing external to the cells. Data from such tests are

considered unreliable.) Three different cycle life tests were initiated and are still in progress. The cell polarization was measured with over 30 different types of oxygen electrodes. The cell polarization was measured at several temperatures for a given pressure and at several pressures for a given temperature. The effects of vibration, shock, and acceleration on performance were also determined. Design, fabrication and testing of a 9 cell unit was carried out during this period.

4. EXPERIMENTAL TECHNIQUES

4.1 Electrode Preparations

Unless otherwise noted, the data presented in this report is based on a cell containing platinized nickel for both H_2 and O_2 electrodes. The polarization studies have, however, included the use of several new types of oxygen electrodes. The details of preparation of these new oxygen electrodes as well as the platinized nickel electrodes are given below:

4.1.1 Preparation of Platinized Nickel Electrodes

The platinized nickel electrodes were prepared by immersion plating of the porous nickel electrode in a 3 percent solution of chloroplatinic acid. The porous nickel, 0.022 in. thick, was obtained from Gould National Batteries and was designated as "raw unimpregnated plates." The amount of solution was fixed on the basis of depositing 40 mg of platinum per square inch of electrode.

4.1.2 Radioactive Electrodes

The radioactive oxygen electrodes were prepared by the Yardney Electric Corporation. Several base materials including porous nickel, platinized porous nickel as well as porous carbon, tantalum and silver were impregnated with radioactive component. Information on the nature of the radioactive component as well as the method of impregnation may be obtained from the Yardney Electric Corporation.

4.1.3 Preparation of Carbon Electrodes

Three types of carbon electrodes have been employed in the oxygen electrode tests. The properties of these carbons are listed below:

<u>Type</u> ¹	<u>Porosity, %</u>	<u>Avg. Pore Size, in.</u>
A	40	0.0027
B	60	0.0055
C	36	3×10^{-5} to 4×10^{-4} (range)

The first step in the preparation of these electrodes was the machining of the proper size electrode, 1-5/8-in. dia., from the sample block. The next step consisted of boiling the electrode in distilled water for 1 hr so as to rid the electrode of loose particles of carbon resulting from the machining step. Each of the electrodes was given the special treatments described below, and then each was evaluated as an oxygen electrode.

- a. Platinum black was applied to a type A electrode, according to the method described by Hunger (3). Briefly, the method consists of brushing a solution of chloroplatinic acid on the electrode and then firing in air to decompose this compound and form platinum black. The amount of solution was based on the deposition of 40 mg of platinum per square inch.
- b. Platinum black was applied to another type A electrode by spreading a moistened slurry of the black over one surface. Approximately 100 mg was added per square inch.
- c. Types A, B, and C were impregnated with a mixture of oxides (spinels), according to Kordes (6). The particular spinel investigated was a silver, cobalt aluminate.

¹Type A and B were obtained from the National Carbon Co. and type C from the Speer Carbon Co.

- d. Type C was activated according to Hunger (3). Briefly, this method consisted of an initial treatment with 50 percent nitric acid, followed by heating for 3 hr at 800°C in a CO_2 atmosphere, (purity 99.95%), as shown in Fig. 1.
- e. Type C was given the same treatment as in the preceding step and in addition, was coated with platinum black, according to Step 1.
- f. Type A was impregnated with various metal oxides by immersion in a concentrated solution of the metal nitrate followed by firing in air at 200°C for 6 hours.

4.1.4 Preparation of Lithiated Nickel Oxide Electrodes

Different types of lithiated nickel oxide electrodes were employed for cells A and B.

For cell A the porous nickel was prepared by the sintering of nickel powder. Metals Disintegrating Company MD151 was screened to obtain the particles between 44 and 74 microns in size. The powder was then placed in an alumina mold and sintered for one hour in a hydrogen atmosphere at 1350°C .

For cell B the porous nickel was the same as that employed in Section 4.1.1.

In both cases however, the lithiating treatment was the same. The porous nickel was first soaked in a lithium hydroxide solution (11.15 gms $\text{LiOH}/100\text{ ml}$) and then fired in air at 750°C for 5 minutes.

4.2 Electrolyte Preparation

The electrolyte consists of a 35% solution of potassium hydroxide impregnated in an asbestos bed. The preparation of this electrolyte bed consisted of cutting two circular discs of $1/32$ inch asbestos sheet and saturating with the KOH solution. The excess solution was removed by repeatedly blotting with a filter paper until the ratio of the weight of solution to weight of dry asbestos was $0.70/1.0$. The amount is also expressed as $2.0\text{ gms solution/in}^2$. The two layers were then compressed together and were ready for insertion within a cell.

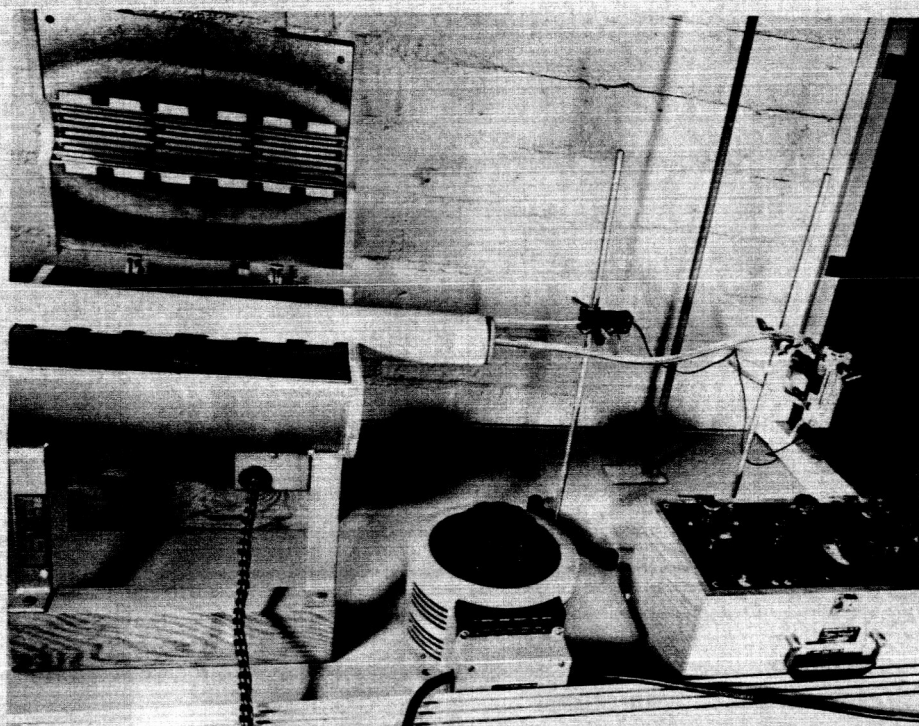


FIG 1
CONTROLLED ATMOSPHERE
FURNACE FOR
ELECTRODE PREPARATION

4.3 Spacers for Multicell

The cell spacers were machined from Plex 55, a special grade of lucite for high temperature operation. The spacers are coated with a conductive layer of nickel approximately 2 mils thick.

The application of the conductive layer is preceded by several steps. First the surface is sand blasted and then cleaned. The surface is then sensitized with a stannous chloride solution and a thin layer of silver is applied by the formaldehyde reduction of an ammoniacal silver solution. Finally, the nickel layer is applied from a sulfamate bath.

4.4 Assembly of Multicell

The assembly of the multicell unit consisted of inserting the electrodes and "O" rings in the appropriate recessed areas of the cell spacers and then stacking the spacers together with an electrolyte layer between each. Special care was taken to be certain that the gas manifold holes were aligned and that the electrodes did not fall out of place. The stack was then placed between the two end plates and bolted together until the distance between spacers was $.035 \pm .005$ inch.

4.5 Temperature, Pressure, and Voltage Measurements

Cell temperatures were measured with a chromel-alumel thermocouple inserted in a small hole in the cell body. A Rubicon potentiometer was used for E.M.F. measurements. Gas pressures were measured with a pressure transducer for the first cell configuration and with precision pressure gages ($\pm 1/2$ percent of full scale) for the second cell configuration. Cell voltages were continuously recorded for all tests with miniature Rustrack recorders.

4.6 Polarization Tests

The total cell polarization was obtained by use of the constant current power supplies. The procedure consisted of setting the current to a given value for either charge or discharge and then measuring the cell voltage on a recorder. After each change in the current setting, a time interval of approximately 3 min was required before a steady state voltage was attained.

4.7 Conduct of Charge Retention Tests

The charge retention tests consisted of charging the cell, heating to the desired temperature and then recording the gas pressures and open circuit voltages at frequent intervals during a 72 hour stand.

4.8 Conduct of Cycle Tests

The cycle life tests were carried out by connecting the cell to a constant current power supply equipped with automatic cycling equipment. The power supply was set at a given current between 0-2 amps for charge and discharge (the current setting could be different for each case). The automatic cycling equipment, designed for the 100 minute cycle, maintained a charge time of 65 minutes and a discharge time of 35 minutes. A small Rustrack recorder was connected to the cell to keep a continuous record of the cell voltage for each cycle.

5. DESCRIPTION OF EXPERIMENTAL CELLS

A description of all the experimental cell models that have been employed in this program is presented in this section. In previous reports (1,2) these cells have been designated as Cell "A", Cell "B" etc.

A brief review of this nomenclature is given below:

Cell "A": This is the initial cell configuration that was employed at the start of the program. The hydrogen is stored in the nickel electrode and the oxygen is stored throughout the porous asbestos bed.

Cell "B": This is the modified cell configuration that has been employed for the major portion of the program. The hydrogen and oxygen are stored in miniature gas cylinders.

Multicell: This is a "scaled up" model of cell "B" above. The unit contains 9 cells in series.

Cell "C": This is known as a "silver-hydrogen" cell. A sub-program was initiated to evaluate this cell during the latter portion of the program. The hydrogen is stored in a small cylinder as in cell "B"; however, the oxygen electrode is replaced by a silver-silver oxide electrode.

5.1 Description of Cell A

The components of cell A are shown in Fig. 2 and are described below:

- a. Hydrogen electrode: sintered porous nickel disc, 15/16 inch diameter, 1/8 inch thick, lightly coated with lithiated nickel oxide.
- b. Oxygen electrode: identical to hydrogen electrode except more heavily lithiated.

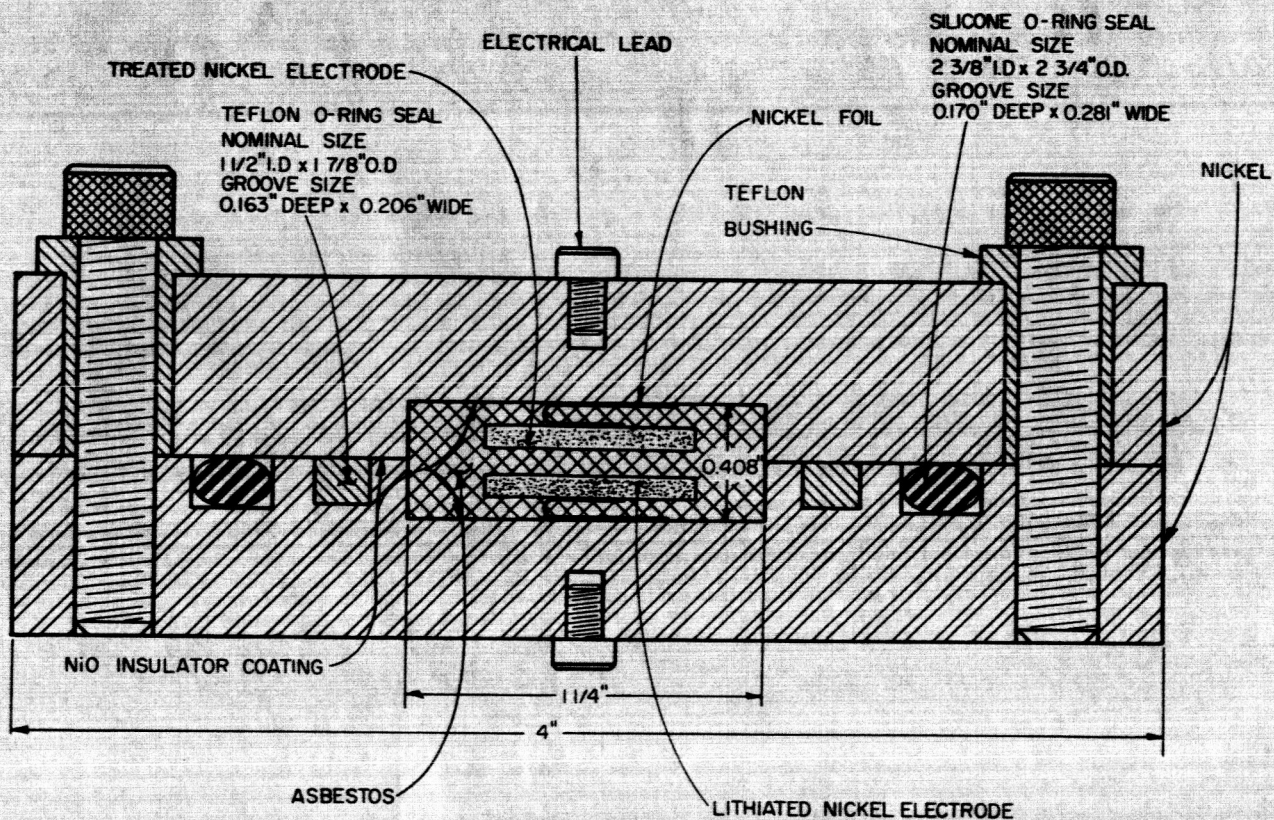


FIG. 2 COMPONENTS OF CELL A

- c. Cell frames: pure nickel, machined to contain electrodes plus asbestos, surface oxidized to form non-conductive nickel oxide.
- d. Internal configuration: electrodes parallel and separated by layer of 1/32 inch thick asbestos; space between electrodes and frames filled in with asbestos; thin nickel strips connected to each electrode and its respective cell frame.

5.2 Description of Cell B

The components of one of the cell B assemblies are shown in Fig. 3. A brief description of these components is given below:

- a. Hydrogen container: 2-in. dia. stainless steel pipe with welded caps.
- b. Oxygen container: same as hydrogen container, except that its volume is 1/2 that of the hydrogen container.
- c. Cell frames: 4-in. dia. stainless steel, recessed for electrodes and O-ring.
- d. Hydrogen electrode: 1-5/8-in. dia., 0.022-in.-thick disc of wire-reinforced sintered nickel, coated with platinum black at 40 mg/in.²
- e. Oxygen electrode: same as hydrogen electrode except where noted.
- f. Pressure gages: 0-100 psig, 0-300 psig, and 0-600 psig.
- g. Electrolyte: 35 percent KOH solutions impregnated in a disc of asbestos 2-1/2 in. dia. by 1/16 in. thick.

The six assemblies are shown in Fig. 4. The components of each assembly are identical except for the volumes of the gas cylinders. The volumes are tabulated below, along with the capacity per unit of pressure at room temperature.

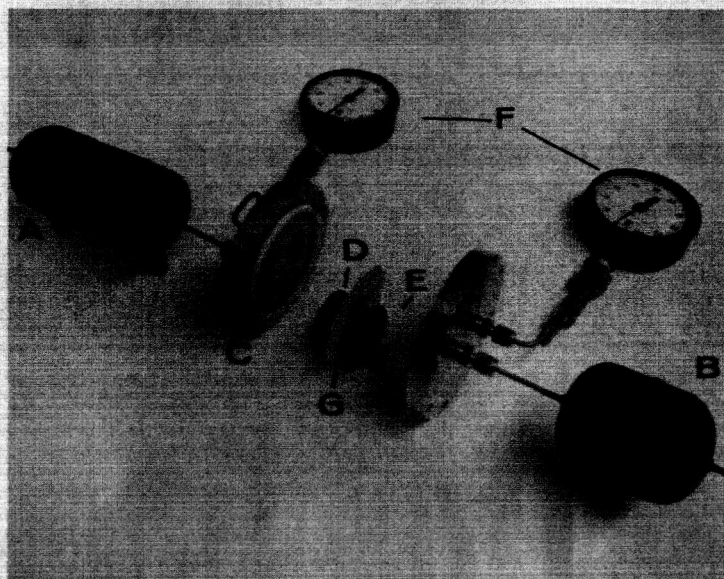


FIG 3
COMPONENTS OF CELL B

- A. Hydrogen container
- B. Oxygen container
- C. Cell frame with "O" ring
- D. Hydrogen electrode
- E. Oxygen electrode
- F. Pressure gages
- G. Asbestos bed

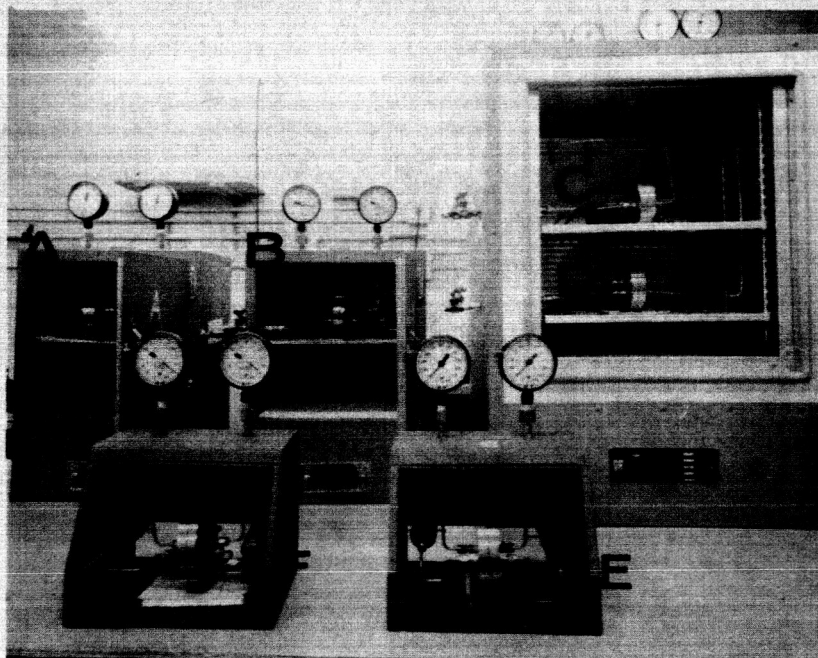


FIG 4
SIX CELL ASSEMBLIES

<u>Assembly</u>	<u>Hydrogen Volume</u>	<u>Oxygen Volume</u>	<u>Capacity amp min/psi at 70°F.</u>
A	270	135	2.38
B	187	94	1.67
C	150	75	1.32
D	140	70	1.24
E	76	38	0.66
F	76	38	0.66

As shown in Fig. 4, four of the assemblies are assembled in ovens for elevated-temperature testing and two in small metal cabinets for room-temperature testing.

5.3 Description of Multicell

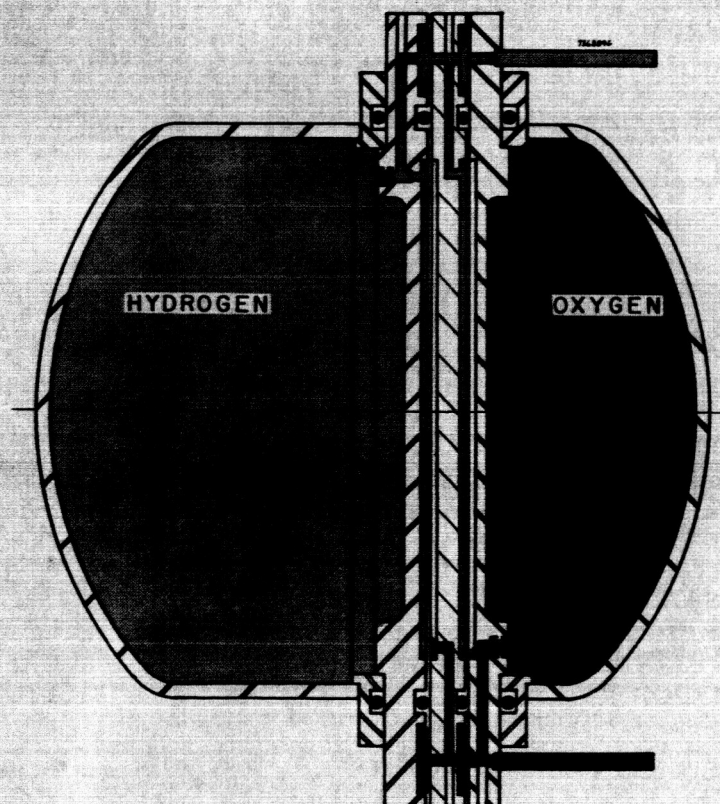
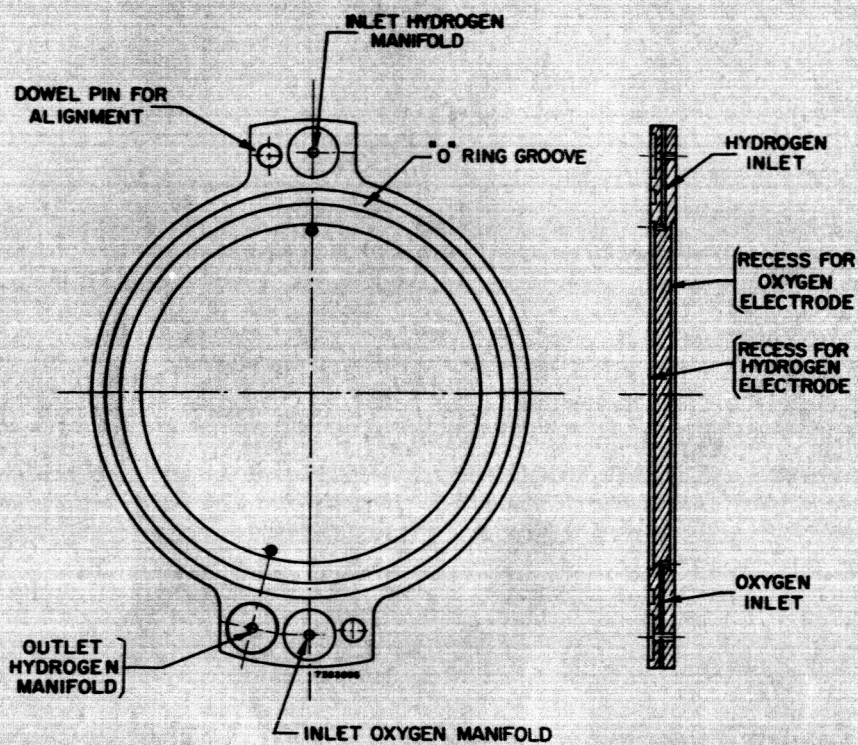
The basic components of the multicell unit are the same as those of the six single cells described above. The electrodes again consist of platenized nickel for both H_2 and O_2 , and the electrolyte bed is prepared in the same manner. The only differences are in electrode size, gas manifolding, and electrical contacts.

An assembly drawing of the multicell unit is shown in Fig. 6. As indicated the two gas cylinders (made of 4 inch diameter stainless steel weld caps) form an integral part of the unit. A flange is welded to each cylinder and contains six bolt holes along its perimeter. Bolts are passed through the flange to connect each cylinder with a steel end plate. The end plates, in turn, contain six bolt holes for holding the entire unit together.

The electrodes are held in place by nickel plated lucite cell spacers shown in Fig. 5. These spacers also serve the purpose of electrically connecting adjacent cells in series and distributing the gases to the electrodes.

Neoprene "O" rings are employed to seal the gas manifolds and the electrode compartments.

Fig. 7 shows the assembled unit under test.



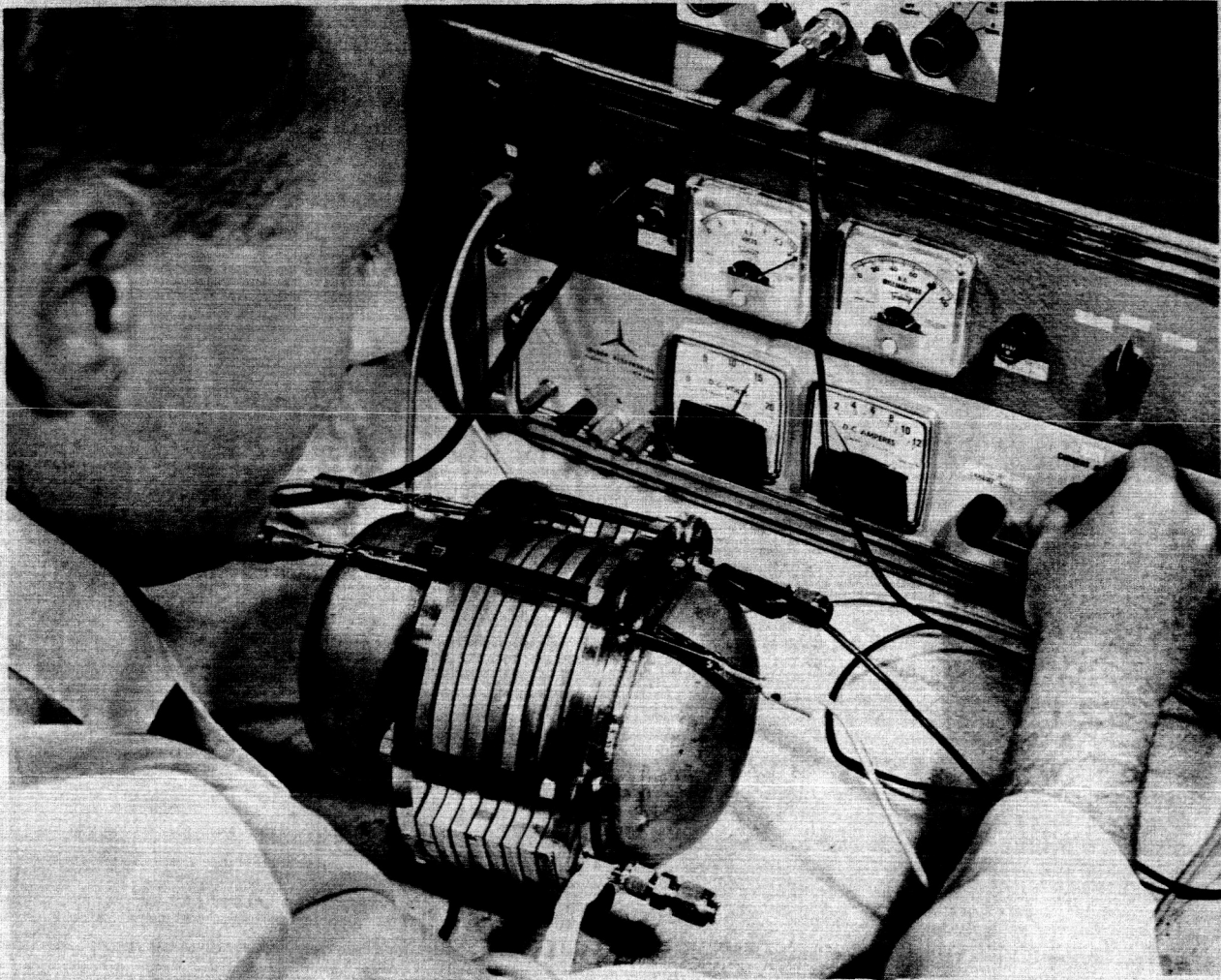


FIG 7 NINE ELEMENT FUEL CELL

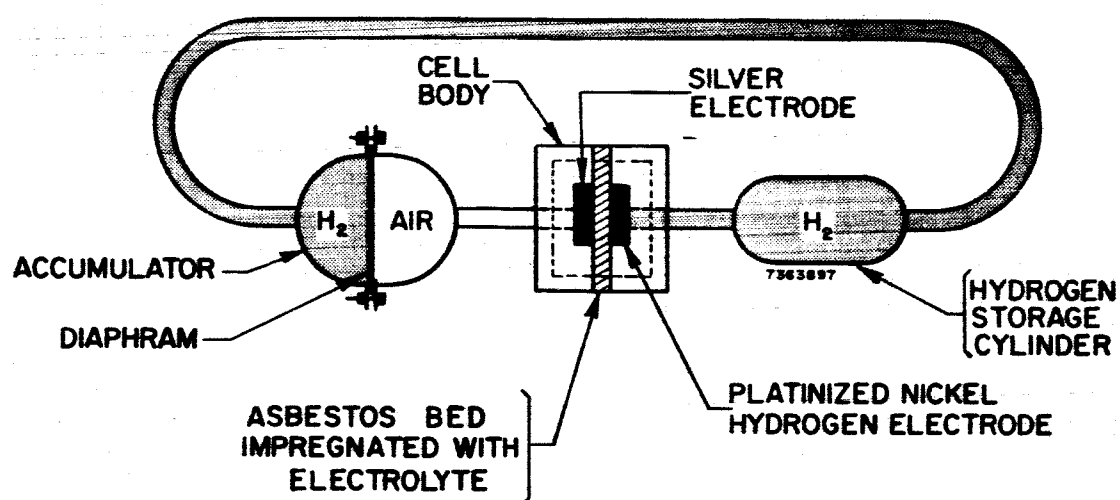


FIG 8 SCHEMATIC OF SILVER HYDROGEN CELL

5.4 Description of Ag-H Cell

A schematic drawing of the Ag-H cell assembly is given in Fig. 8. The essential components are the cell, the hydrogen storage cylinder and an accumulator.

The cell consists of a silver-silver oxide electrode, an electrolyte of KOH solution impregnated in an asbestos bed, and a hydrogen electrode. The silver electrode was taken from a silver-zinc battery. The platinized nickel hydrogen electrode is the same as that employed for cell "B". The electrolyte bed is also prepared in the same manner as for cell "B".

Pressure equalization across the asbestos bed is accomplished via the use of an accumulator. The operation of this accumulator is readily apparent after inspection of Fig. 8. On charge the build up of hydrogen pressure displaces the diaphragm within the accumulator which, in turn, compresses the air on the other side so as to equalize the pressures on either side of the bed.

6. RESULTS AND DISCUSSION

The results of the experimental program are presented in the following three sections. The first section deals with the evaluation of the proposed H_2-O_2 cell. The second gives the results of the investigations of the modified cell. The third section given the results of the preliminary evaluation of a silver-hydrogen cell.

6.1 Characteristics of Cell A

The results of the investigations of the initially proposed cell are given in the following subsections.

6.1.1 Polarization Characteristics

The voltage-current curve of this cell is given at three temperatures in Fig. 9. As indicated the polarization for both charge and discharge is appreciably reduced by an increase in temperature. At room temperature the polarization is so large that the short circuit current is but a few ma/cm^2 .

6.1.2 Cycle Life

Extensive cycle life testing was not carried out on this cell. However, the cell was carried through 168 continuous cycles over a 10 day period without any apparent deterioration. On the 10th day the cell was destructively tested by excessive overcharging.

6.1.3 Effect of Parameters on Cycling Performance

The following results are based on the 100 minute cycle:

- a. Current efficiency was found to be markedly dependent on temperature. The efficiency was found to first increase and then decrease as the operating temperature was raised. A maximum efficiency of 65 percent was found at a temperature near $278^{\circ}F$.

- b. Current efficiency was also found to be markedly dependent on the electrolyte content of the asbestos bed. The efficiency was found to first increase and then decrease as the electrolyte level was increased. A maximum efficiency near 65 percent was found at an electrolyte level near 0.90 cc of 35 percent KOH solution per gram of asbestos.
- c. Voltage efficiency was found to increase with operating temperature. The maximum attained was 68 percent, at a temperature near 340°F.

6.2 Characteristics of Cell "B"

The characteristics of cell B are presented in the following subsections.

6.2.1 Charge Retention

Charge retention tests were conducted at various conditions of temperature and pressure to determine the effect of these parameters on self discharge.

a. 30 Day Stand

The results of a 30 day stand test at room temperature are shown in Figures 10 and 11. Figure 10 gives the variation in the two gas pressures during the stand. As indicated, the decline is so small as to be almost negligible. Figure 11 gives the discharge characteristics of the cell at the end of the 30 days. The current X time output of 1.82 a.h. was 91 percent of the input of 2.00 a.h.

b. 72 Hour Stands

The results of numerous 72 hour stand tests at various conditions of temperature and pressure are given in Figure 12. This curve correlates the charge retention characteristics of the cell, expressed in terms of percent lost per hour, with the ambient temperature. Analysis of this curve establishes the following relationships:

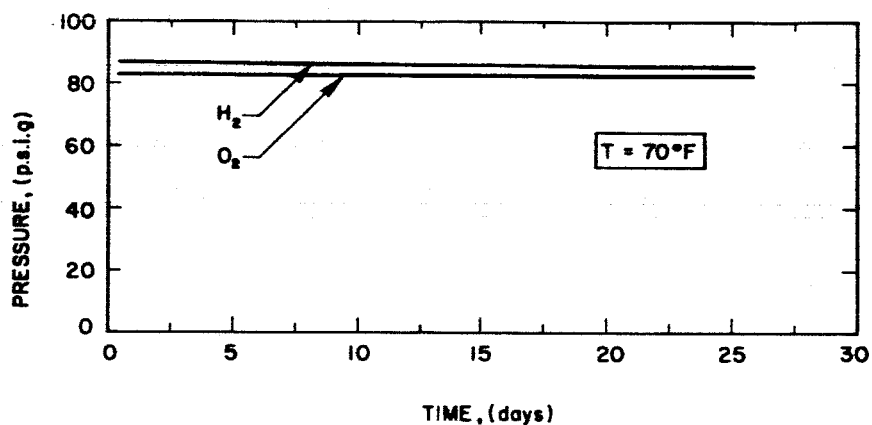


FIG 10 30 DAY CHARGE RETENTION TEST

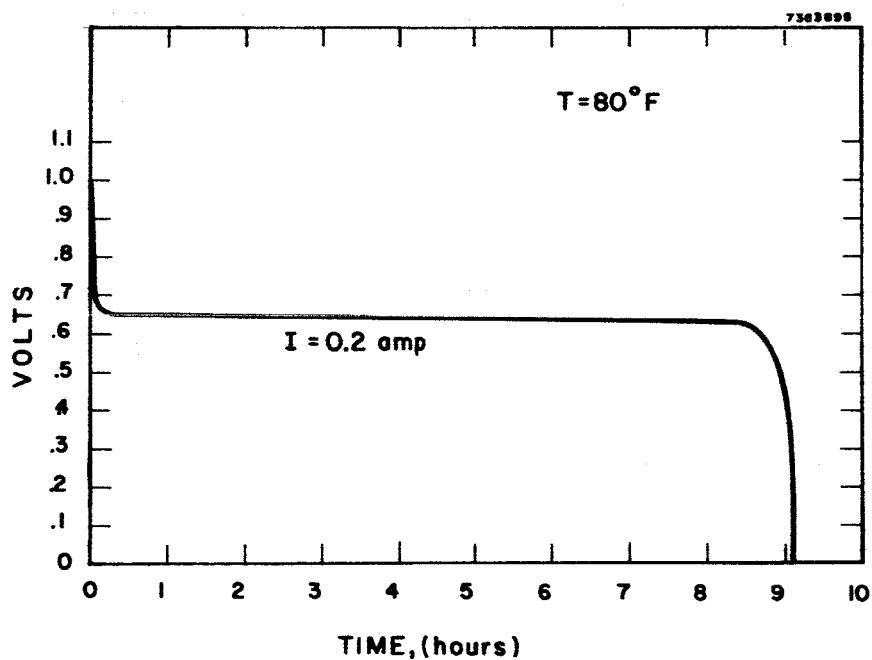


FIG 11 DISCHARGE CHARACTERISTICS AFTER
30 DAY STAND

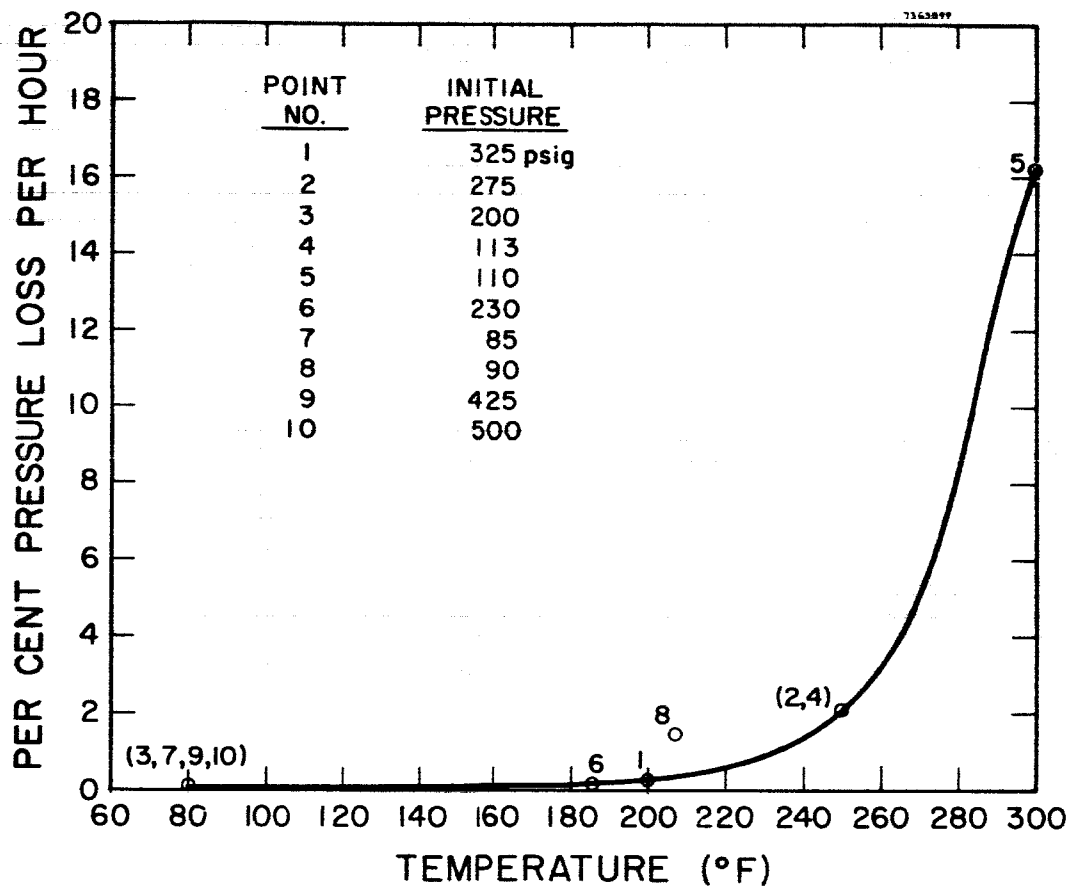


FIG 12 CHARGE RETENTION AS A FUNCTION OF TEMPERATURE AT VARIOUS PRESSURES

1. Effect of Temperature at 200°F

Temperature has very little effect on charge retention from 70°F to approximately 200°F. Within this range the cell retains over 90 percent of its charge for stand times of at least 3 days. Based on the results of Section a above, this statement may be amended to read 30 days at room temperature. Further examination of Figure 12 indicates that at temperatures below approximately 170°F the loss is essentially zero for a 3 day stand.

2. Effect of Temperature Beyond 200°F

As indicated in Figure 12 the rate at which the cell loses its charge increases rapidly with temperature beyond 200°F.

3. Effect of Pressure

Charge retention appears to be nearly independent or at least a very weak function of pressure to 500 psig (the maximum used to date). The four room temperature tests 3, 7, 9, and 10 show for example that the charge retentions are identical and equal to nearly 100 percent at pressures of 85, 200, 425, and 500 psig. Comparison of the two elevated temperature tests 2 and 4 at 250°F shows however that pressure has a slight effect at this higher temperature, i.e., the rate at which the cell loses its charge increases slightly with an increase in pressure.

6.2.2 Polarization Studies

The results of the various polarization studies are given in the following subsections.

a. Oxygen Electrode Evaluation

The objective of the oxygen electrode studies was to find an electrode which showed less polarization than the currently employed platinized nickel.

The evaluation consisted of the measurement of total cell polarization using various oxygen electrodes. Platinized nickel was used as the hydrogen electrode in all tests and thus any differences would be directly attributable to the oxygen electrodes.

Figure 13 shows the cell polarization as a function of various types of oxygen electrodes. As indicated by curve 1 the polarization of the electrode specially prepared by a battery manufacturer is much less than that of all the others which were investigated.

The lithiated nickel oxide was found to show much less polarization at 200°F (curve 5) than at room temperature (curve 6) due to its properties as a semiconductor. (4)

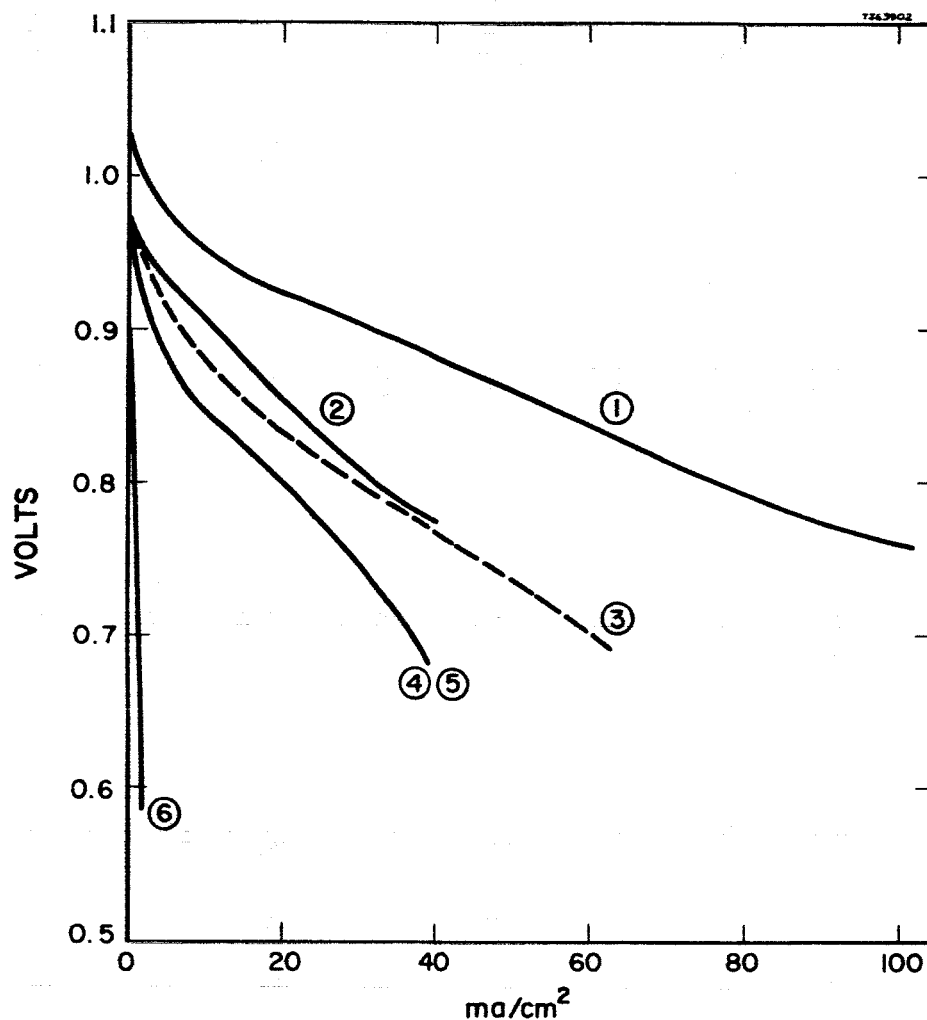
The platinized carbon electrode (curve 2) showed excellent polarization characteristics especially at low current densities, but showed a deterioration in performance with time.

The polarization curves of all other carbon electrodes listed below fell within the area between curves 5 and 6.

1. Type B + spinels (See 4.1.3c)
2. Type A + spinels (See 4.1.3c)
3. Type C unactivated (See 4.1.3)
4. Type C activated (See 4.1.3d)
5. Type A + copper oxide (See 4.1.3f)
6. Type A + cobalt oxide (See 4.1.3f)
7. Type A + chromium oxide (See 4.1.3f)
8. Type A + nickel oxide (See 4.1.3f)
9. Type A + iron oxide (See 4.1.3f)

b. Effect of Pressure on Polarization

During the course of the charge-retention tests, the observation was made that the discharge voltage appeared to be sensitive



- | | |
|---|---|
| ① Special Electrode from a battery supplier; 30 psig, 150°F | ④ Platinized Carbon, Type A; 50 psig, 200°F |
| ② Platinized Carbon, Type C; 50 psig, 200°F | ⑤ Lithiated NiO; 30 psig, 200°F |
| ③ Platinized Nickel; 80 psig, 200°F | ⑥ Lithiated NiO; 30 psig, 80°F |

FIG 13 OXYGEN ELECTRODE EVALUATION

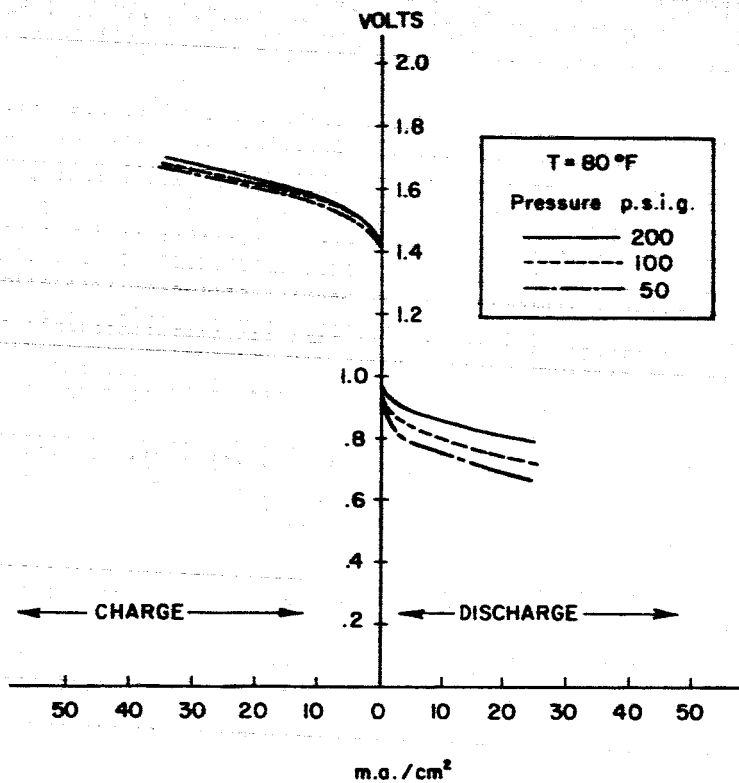


FIG 14 EFFECT OF PRESSURE ON POLARIZATION

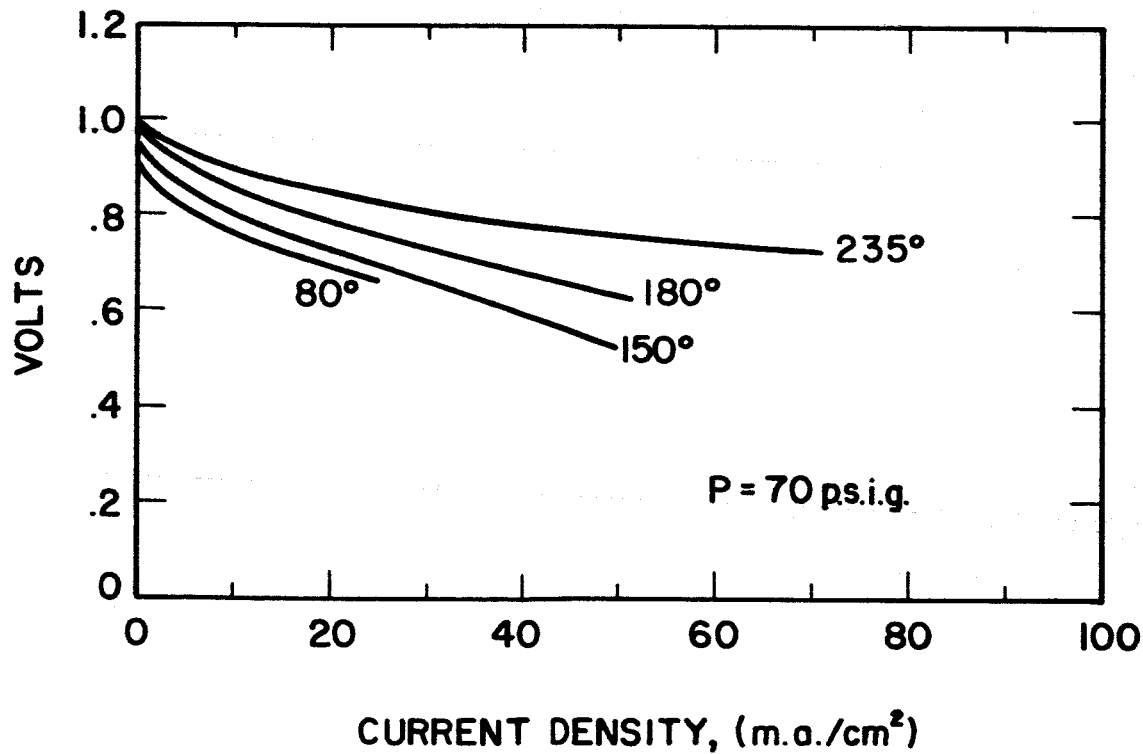


FIG 15 EFFECT OF TEMPERATURE ON DISCHARGE POLARIZATION

to the gas pressure. Consequently, an examination of this relationship was undertaken.

Figure 14 gives the room-temperature polarization for both charge and discharge at three different pressures. Inspection of this figure reveals that the discharge voltage is markedly dependent upon pressure. For example, if the pressure is increased from 50 to 200 psig, the discharge voltage increases by approximately 0.1 volts at 20 ma/cm². The charge voltage is also found to be dependent upon pressure, but in this case, the effect is not as pronounced.

c. Effect of Temperature on Polarization

The voltage-current curve of cell B is given as a function of temperature in Figure 15. As indicated, the operating temperature has a marked effect on polarization. For example if the temperature is raised from 80°F to 180°F, the discharge voltage increases by approximately 0.1 volt at 20 ma/cm².

6.2.3 Cycle Life Testing

Three cycle life tests have been carried out in order to ascertain the adverse effects, if any, of continued cycling on cell performance.

a. 65/35 Cycle at 70°F

This cycle test has consisted of a 65 minute charge at 125 ma and a 35 minute discharge at 200 ma. Automatic cycling equipment has been employed to run the test on a continuous 24 hr/day basis. Cycling was initiated in November, discontinued for a time in January, and continued again in February until the present time. The discontinuation occurred at the end of the 417th cycle at which time the voltage dropped suddenly to zero in the middle of a discharge period. The cause for the voltage fall was attributed to an external short circuit in the assembly. Disassembly and examination of the cell revealed no apparent deterioration of the electrodes and the weight of the asbestos bed indicated a very low loss of water. The cell was reassembled with the same components and started cycling again. Although the charge and

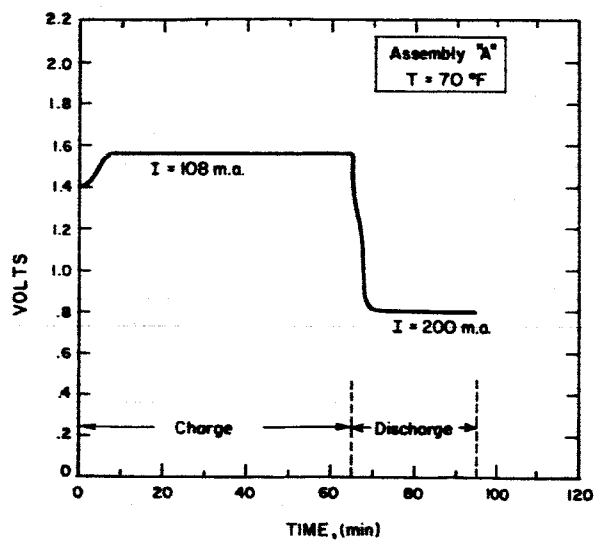


FIG 16
TYPICAL 65/35 CYCLE AT 70°F

FIG 17
TYPICAL 60/300 CYCLE

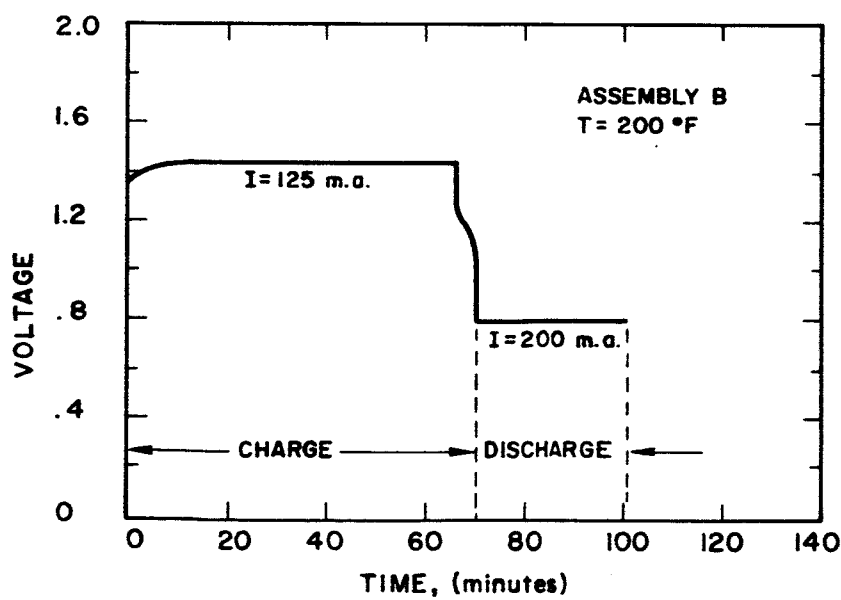
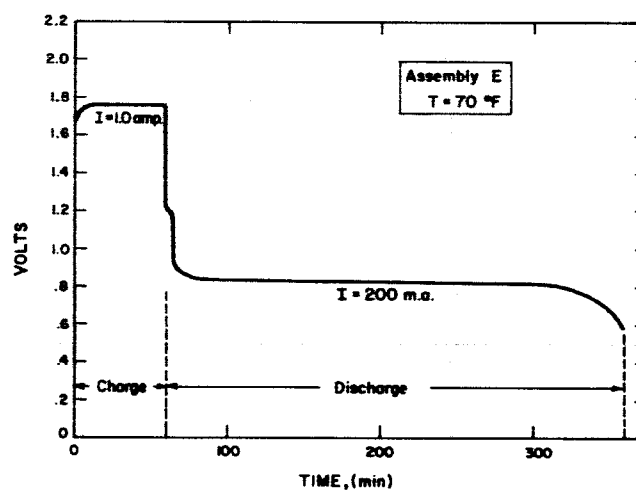


FIG 18
TYPICAL 65/35 CYCLE
AT 200°F

discharge voltages were found to be somewhat different than for the first 417 cycles, they have been constant for the past several hundred cycles. Because of minute gas leaks the charge current has been increased and the discharge current decreased. The voltage for a typical cycle is given in Figure 16 . Altogether the cell has completed over 1100 cycles for an operating time of more than 1800 hours.

b. 60/300 Cycle at 70°F

This cycle has consisted of a 60 minute charge at 1.0 amp and a 300 minute discharge at 0.2 amps. This test has been conducted on a semi-continuous basis, i.e. one 6 hour cycle per day.

This particular cycle employs a greater "depth" of discharge than the above 65/35 cycle; i.e. a greater percentage of the water is removed from the bed via electrolysis and the build up of gas pressure is correspondingly higher.

Cycling was initiated in January and has been continued until the present time. Altogether the cell has completed 70 cycles for an operating time of 116 hours. The charge and discharge voltages have been nearly identical from cycle to cycle indicating no deleterious effect of cycling on performance. The voltage for a typical cycle is given in Figure 17.

c. 65/35 Cycle at 200°F

This test was initiated during the last month of the program and has been in progress to the present time. The cycle is identical to the one in Section 6.2.3.a except that the operating temperature has been maintained at 200°F (versus 70°F in the above test). To date the cell has completed 160 cycles. The voltage as shown in Figure 18 has remained constant from cycle to cycle.

6.2.4 Capacity

The theoretical capacity of the cell is related to the water content of the asbestos bed. This capacity is equal to the weight of the water times the electrochemical equivalent of the water (approximately 3a-h/gm). Based on the water content of the bed (Sec. 4.2) the theoretical capacity, expressed in terms of unit area, is 3.9 amp-hrs/in².

In practice however, this theoretical capacity cannot be obtained for if all of the water were electrolyzed from the asbestos bed, the beds' resistance to gas flow would be less, resulting in a rapid gas mixing and subsequent self discharge of the cell.

Analysis of the charge retention tests indicates that for reasonably good charge retention characteristics (less than 1 percent loss after 3 days) the amount of water that can be electrolyzed from the bed is approximately 0.67 gms/in^2 and the corresponding capacity is 2.0 amp-hrs/in^2 .

6.2.5 Environmental Testing

A series of environmental tests was conducted on the cell at the Jet Propulsion Laboratory. These tests were intended to simulate flight environment conditions in both the boost-phase and space flight phase of the Mariner spacecraft program. The cell operated perfectly while on both charge and discharge throughout the testing program. For all the tests in the series the charging current was 1.0 amp and discharging current 100 milliamps.

A brief description of each test is given below and the performance of the cell prior to and following the test series is shown in Figures 19 and 20.

a. Static Acceleration

This test simulates conditions encountered by the spacecraft during booster burning. The test was carried out in accordance with JPL Spec. 30250, paragraph 4.3.1. The cell was subjected to a static acceleration along the thrust axis in a forward direction of 14g for 5 minutes and 4g for 5 minutes in the reverse direction. Finally, it was given 6g for 5 minutes in the orthogonal direction.

b. Vibration

The following tests were intended to simulate damaging effects due to structural excitation and acoustic coupling during booster burning. The test was divided into two parts, that of low frequency and high frequency vibration.

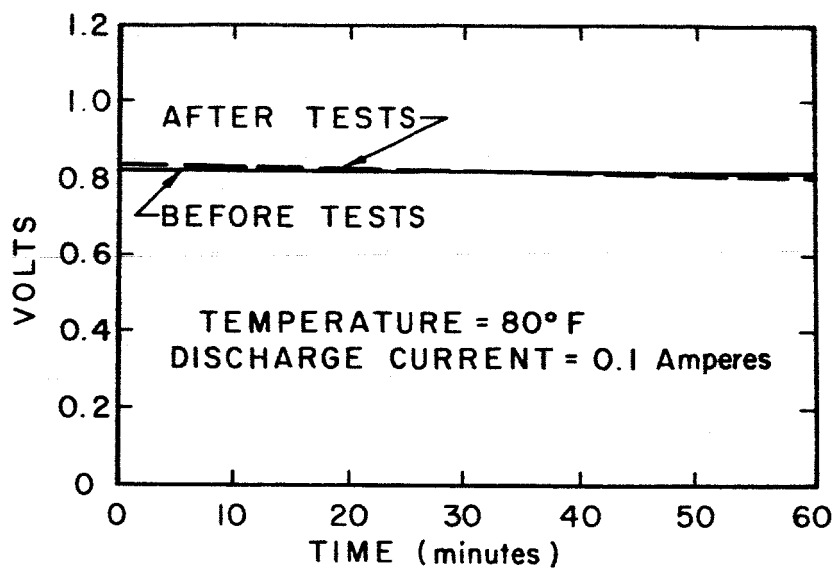


FIG 19 VOLTAGE VS TIME BEFORE AND AFTER ENVIRONMENTAL TESTS

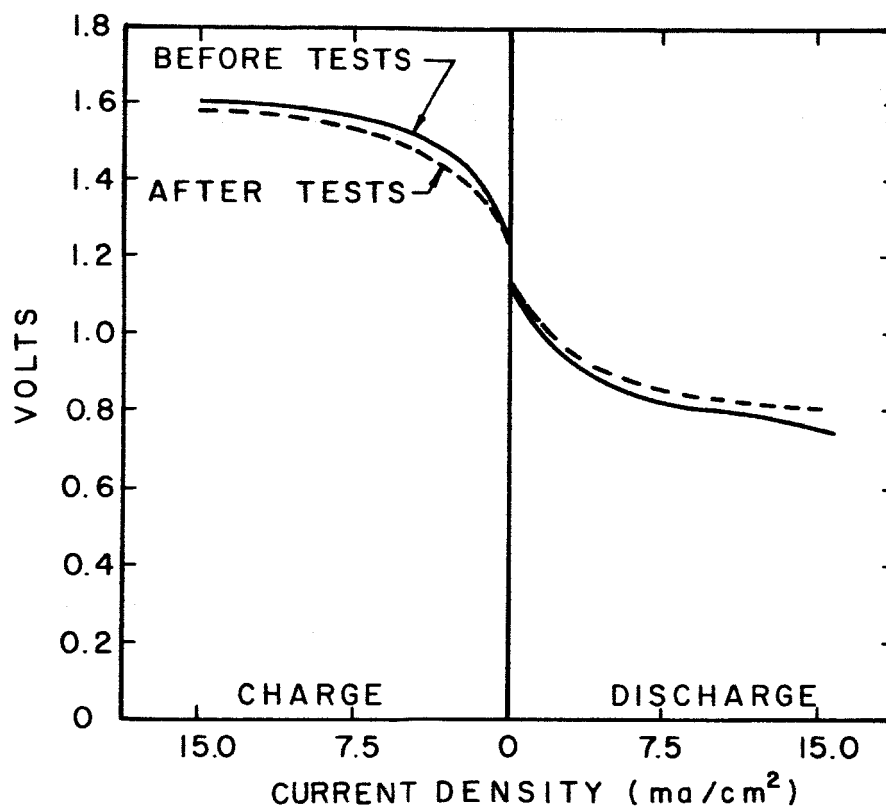


FIG 20 POLARIZATION BEFORE AND AFTER ENVIRONMENTAL TESTS

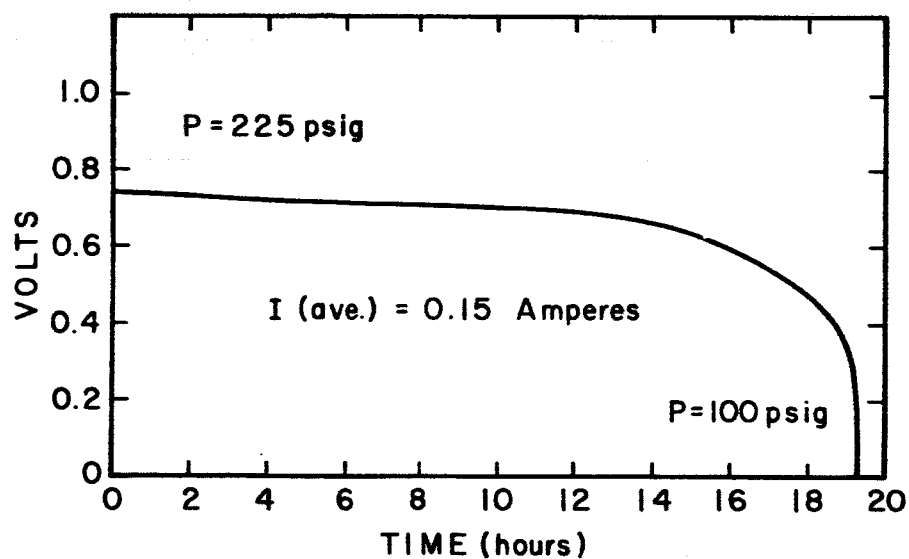
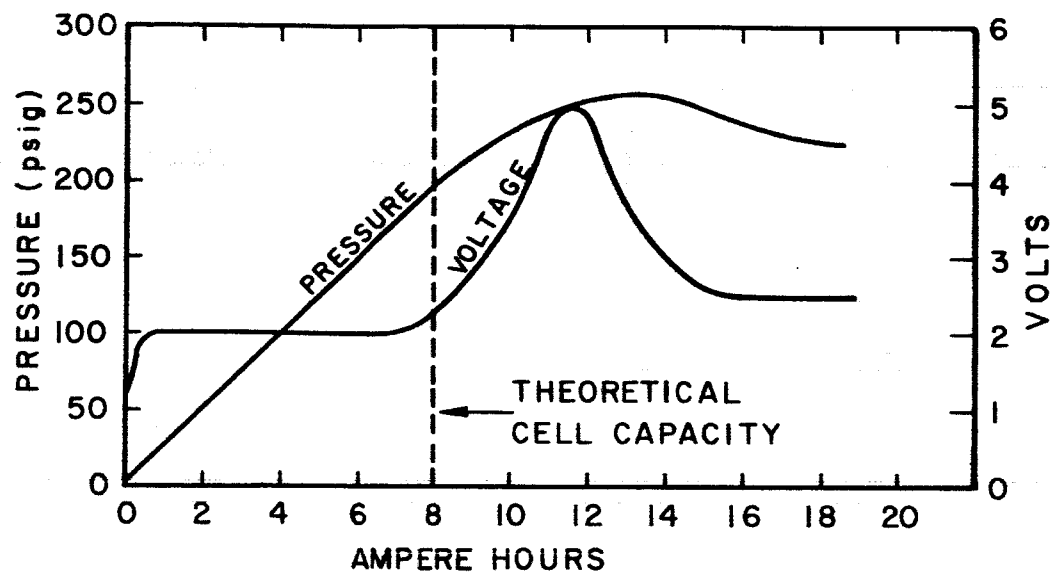


FIG 21 DISCHARGE CHARACTERISTICS AFTER OVERCHARGE

1. Low frequency vibration:

This test was conducted according to JPL Spec. 30250, paragraph 4.3.2.11. The cell was subjected to sinusoidal frequencies between 1 and 40 cps for 24 minutes in the two orthogonal directions.

2. High frequency vibration:

This test as outlined in JPL Spec. 30250, paragraph 4.3.2.1.2, consists of a programmed sequence of band-limited white Gaussian noise and combined noise and sinusoidal vibration.

c. Shock

The following test was intended to simulate the high frequency-high amplitude shocks associated with separation from the launch vehicle. In accordance with JPL Spec. 30250, paragraph 4.4.1, it consisted of two 200g, 0.5 to 1.5 millisecond shocks, parallel and perpendicular to the thrust axis.

6.2.6 Effect of Overcharge

In order to test for potential safety hazards involved in the operation of the cell, assembly A was given an excessive charge i.e. an input greater than that required to electrolyze all of the water from the asbestos bed.

The variation of both gas pressures and cell voltage with input are shown in Fig. 21. The vertical dashed line near 8.0 amps-hrs corresponds to the input required to electrolyze all of the water in the bed.

Inspection of Fig. 21 reveals that the cell voltage remained constant at 2.0 volts for the first 8.0 amp-hrs of input. This voltage is in accordance with the room temperature polarization data for the indicated charging current of 2.0 amps (150 ma/cm^2). The gas pressures were also found to increase linearly with input, as is usual, to 8.0 amp-hrs.

As the charge was increased beyond 8.0 amps-hrs the cell voltage was found to first increase sharply, then decrease, and

finally level off at 2.5 volts. The gas pressures were found to increase at a slower rate, then decrease and level off at a lower value. The cell temperature, not shown, varied in accordance with the gas pressure i.e. increased from room temperature to a maximum of 44°C and then leveled off near 35°C.

The results of this test indicate that an excessive charge does not cause any safety hazard i.e. an explosion. The gases undoubtedly recombine chemically to form water but the recombination rate is not fast enough to be explosive in nature. The mechanism of recombination most likely involves the diffusion of one gas through the asbestos bed and chemical recombination with the other gas on the surface of the platinized nickel electrode.

The discharge characteristics of this cell after the overcharge test are shown in Fig. 21. Due to a lack of power supplies at the time of this test the discharge was carried out with a rheostat. Consequently the discharge current was not constant i.e. 0.2 amp at the start and 0.1 amp at the end. Assuming an average current of 0.15 amp the output is found to be 1.85 amp-hrs, or 0.925 amp-hrs/in².

6.2.7 Effect of Sudden Pressure Release

In order to gain more information concerned with the possible safety hazards involved in the operation of the cells being developed, the following tests were conducted with assembly B containing platinized nickel electrodes.

- a. The cell was charged at room temperature for a period of time such that the H₂ and O₂ pressures were near 100 psig. At this point, the H₂ cylinder was opened to the atmosphere, permitting the H₂ gas to escape and the H₂ pressure to return to 0 psig. Then, the H₂ cylinder was closed. After a few minutes, the O₂ pressure began to decline and the H₂ pressure began to rise, indicating the transfer of

O₂ into the H₂ cylinder. After several minutes, the two pressures were nearly equal.

During the whole course of this run no explosion took place.

- b. The same experiment as in "a" was conducted, except that in this case, the O₂ cylinder was opened to the atmosphere. As before, no explosion occurred.
- c. Experiments "a" and "b" above were repeated at 200°F. As before, no explosion was found to occur in either case.

6.2.8 Effect of Pressure Differential

During the early stages of investigation of cell B the cell voltage was found on occasion to drop suddenly to zero in the middle of a discharge period. Observation indicated that the voltage drop was always accompanied by a large pressure differential between the H₂ and O₂.

Consequently a study was made of the effect of pressure differential on discharge voltage. The study consisted of operating the cell as a primary (supplying the gases from external cylinders) and manually applying a pressure differential while the cell was on discharge.

The results of this study indicated that if the pressure differential (H₂ greater than O₂ or vice versa) is less than approximately 10 psig the cell voltage is stable. When the differential is greater than this value however, the voltage drops suddenly to zero.

Design of this cell for a given application must take this result into account. The volume ratio of the H₂ and O₂ cylinders must be as close as possible to 2/1 in order that the pressure differential be less than 10 psig when the cell is charged to a pressure of say 500 psig. If the volume ratio is not precisely controlled, then use may be made of a pressure equalizer to keep the differential within the 10 psig limit. Such an equalizer (See Section 5.4) may readily be incorporated within the system.

6.2.9 Multicell

The characteristics of the 9 cell unit are described below.

a. Polarization Characteristics

The voltage-current characteristics of the unit are given in Figure 23. The V/I data, when expressed in terms of volts per cell versus current density, corresponds to within 10 percent of the same data for the small single cell lab models. Hence, there is no scaling effect due to the size of this unit.

b. Discharge Characteristics

The discharge voltage-time curves for the unit are presented in Figure 22. The slight decline in voltage with time can be attributed to the decrease in pressure (see Section 6.2.2b).

The phenomena of cell reversal was observed on several occasions during discharge. At these times the voltage of one of the 9 cells was found to drop suddenly to zero and then become negative (0.2 to 0.8 volts).

This phenomena can be explained on the basis of a faulty cell which cannot maintain a voltage as high as the other cells and is subsequently given a negative charge by them.

The inability of the cell to maintain its voltage is attributed to one or more of several controllable factors. One such factor may be gas starvation brought about by a restriction in the inlet manifold. Another such factor is an inactive electrode caused by a faulty platinization step. High intercell resistive resistances and poor electrode - electrolyte contact i.e. the electrode is not flush against the asbestos bed, are two additional factors.

Future development on this and subsequent units should take these factors into account. Extensive testing should be carried out before assembly of the unit to insure that all cells are identical and thereby eliminate the possibility of cell reversal.

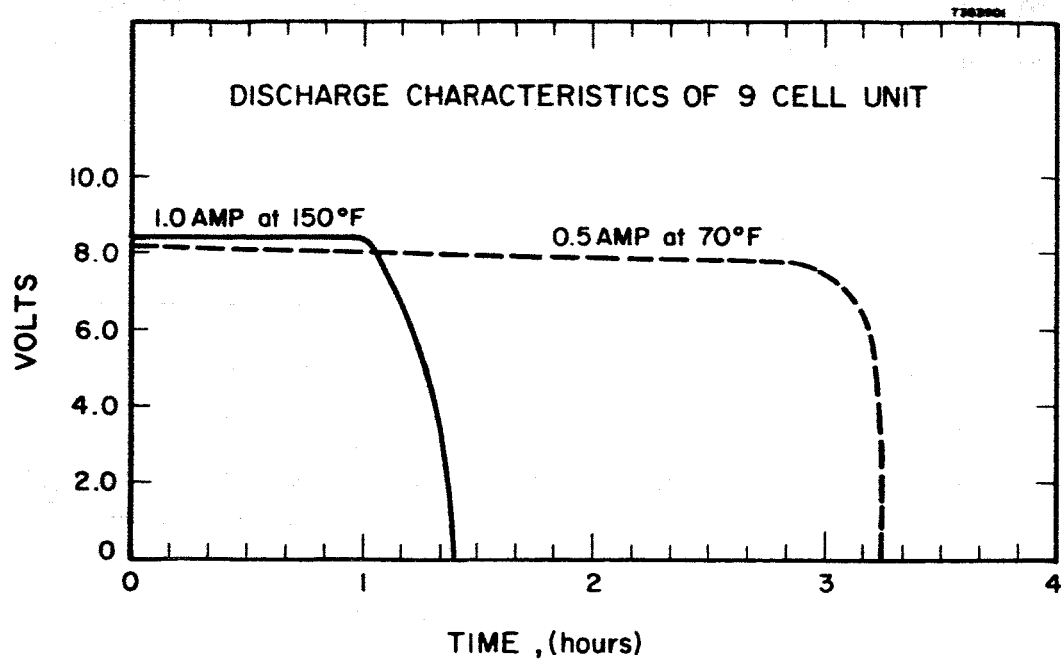


FIG 22 VOLTAGE VS TIME AS A FUNCTION OF TEMPERATURE

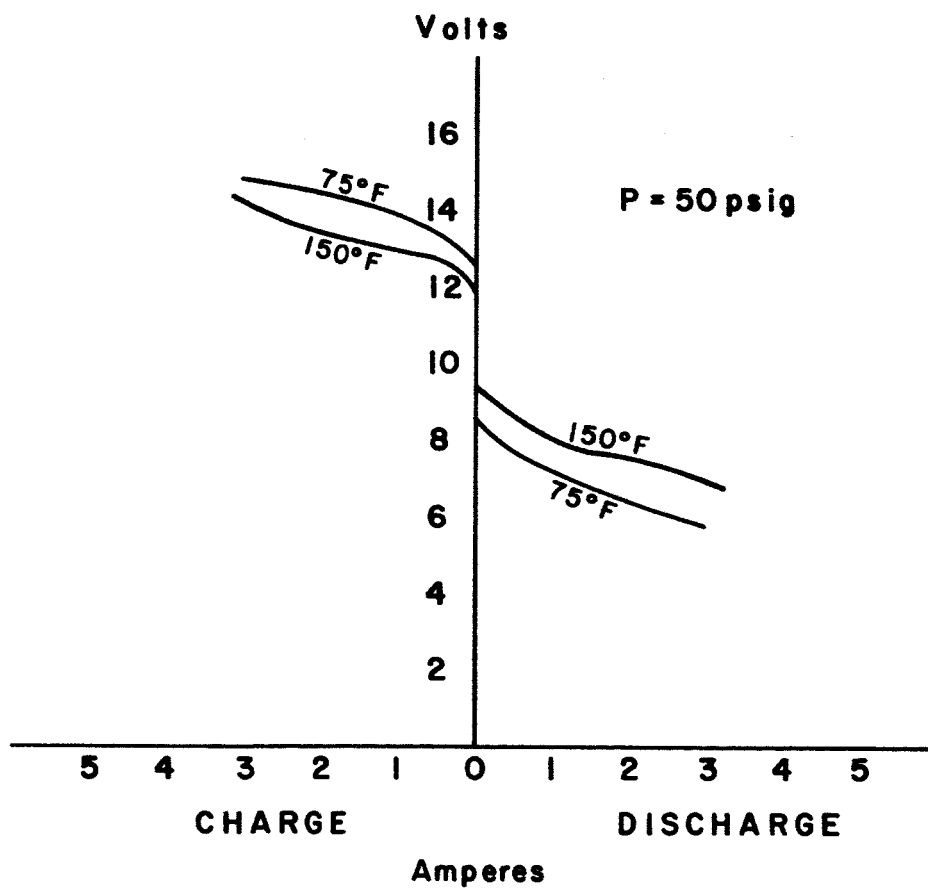


FIG 23 POLARIZATION OF 9 CELL UNIT

c. Power Output

The power output of the unit at two temperatures is tabulated below:

T = 70°F

Volts	Amps	Watts
9.0	0.0	0.0
8.0	0.2	1.6
7.6	0.5	3.8
6.9	1.0	6.9

T = 150°F

Volts	Amps	Watts
9.3	0	0.0
8.7	.2	1.7
8.2	.5	4.1
8.0	1.0	8.0
7.7	2.0	15.4
7.0	3.0	21.0
6.2	4.0	24.8

d. Weight

The total weight of the 9 cell unit is 10.5 lbs. Of this total the fuel cell portion accounts for 2.0 lbs. while the balance, 8.5 lbs., is due to the weights of the gas cylinders, end plates, fittings, bolts and nuts. The major portion of the total weight is thus seen to be associated with these non-fuel cell components.

An appreciable reduction in total weight can readily be accomplished by redesigning the non-fuel cell components. The gas cylinder for example could be made much thinner. On the basis of the equation for a thin walled pressure vessel the required thickness may be calculated as follows:

$$t = \frac{PxD}{2S} \times \text{Safety Factor where: } t = \text{thickness, inches}$$

P = internal pressure
psi

D = diameter, inches

S = allowable stress
psi

Given all allowable stress of 100,000 psi, a diameter of 4 inches, and an internal pressure of 400 psi, the required thickness with a safety factor of 4 is approximately 1/32 inch. The actual thickness of 1/4 inch is thus seen to be 8 times greater than is necessary. Considering that the material of construction is steel, the use of a thinner section would result in an appreciable weight saving. Similarly the end plates which consist of 5/16 inch steel can be shown to be over designed. Smaller fittings could be employed and the heavy bolts could be replaced by a strap.

These weight saving features were not brought into the original design, because at that time it was felt that the emphasis of the program should be the rapid development of a reliable working model. Now that the unit has reached this stage of development, these and other modifications to lower its weight and improve overall performance and design can be introduced.

6.3 Characteristics of Cell C

A limited amount of data has been obtained on the characteristics of the silver-hydrogen cell. The investigations to date have been of an exploratory nature.

The cell appears to offer a potentially high power efficiency as indicated by the following data for a room temperature cycle:

Charge current	50 ma
Charge voltage	1.16 volts
Charge time	2.1 hrs
Discharge current	50 m.a.
Discharge voltage	1.12 volts
Discharge time	2.0 hrs

Voltage efficiency	96.5 percent
Current efficiency	95.0 percent
Power efficiency	91.7 percent

Although the cell operates at high efficiency its feasibility may be limited by its charge retention characteristics. The first test results indicated a very high self discharge rate of 0.2 percent/hr at room temperature and 1.9 percent/hr at 60°C. The cause for the high self discharge is not known at the present time.

7. CONCLUSIONS

The high self discharge rate of cell A would limit the application of this cell to the condition of continuous cycling with total cycle time of less than two hours. The operating temperature would have to be maintained between 200 and 300°F.

The self discharge rate of cell B is essentially zero from room temperature to 170°F and pressures to 500 psig. Nearly 100% of the charge is retained for at least 3 days. At room temperature the cell retains nearly all of its charge for at least 30 days.

The self discharge rate of cell B increases rapidly with temperature beyond 200°F. The loss is for example 0.5%/hr at 210°F, and 2.1 %/hr at 250°F. The loss could be compensated for by a "trickle charge" at these elevated temperatures.

Cell B with platinized nickel electrodes for H₂ and O₂ can complete at least 1100 shallow cycles and at least 70 deep cycles at room temperature without appreciable loss in performance. At 200°F the cell can complete at least 150 cycles without any loss in performance.

The radioactive treated oxygen electrode exhibits significantly less polarization than any of the 30 different types that were examined. A platinized nickel oxygen electrode exhibits somewhat more polarization than the radioactive one, but somewhat less than most of the others. One type of platinized carbon is equivalent to the platinized nickel as an oxygen electrode.

Both pressure and temperature have a marked effect on the polarization of cell B with platinized nickel electrodes for both H₂ and O₂. An increase in pressure reduces the discharge polarization markedly and the charge polarization to a lesser extent. An increase in temperature markedly lowers both charge and discharge polarization.

The performance of a multicell unit with large diameter electrodes can be reliably predicted on the basis of the performance of single cells with small diameter electrodes if all cells are identical. If all cells are not identical then the phenomena of cell reversal can occur.

Cell B can withstand excessive overcharge without causing any safety hazard. The cell can also deliver at least 0.92 a-h/in² after an excessive overcharge.

Cell B can withstand a sudden release of either of the gases without causing any safety hazards at both room temperature and 200°F.

The silver-hydrogen cell exhibits exceptionally high voltage efficiencies.

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